The thermal diffusion in binary gaseous mixtures under pressures, III : hydrogen-argon system

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THE THERMAL DIFFUSION IN BINARY GASEOUS MIXTURES UNDER PRESSURES, III

Hydrogen-Argon System

By Tadashi Makita and Toshiharu Takagi

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The thermal diffusion in the hydrogen-argon system has been measured at mean temperatures of 322.7~352.1°K and pressures up to 220 atm, by means of a "two-bulb" type apparatus reported previously. The effect of composition, temperature and pressure on the thermal separation and the thermal diffusion factor is discussed and compared with the results of the hydrogen-carbon dioxide system in earlier works. The results at the atmospheric pressure are also compared with a theoretical equation treated with both Lennard-Jones (12-6) and "Modified Buckingham" (exp-6) potentials.

There have been only a few studies of the thermal diffusion in gaseous system under high pressures, in spite of its importance for both practical use and theoretical treatment, as described in the author's review paper[1]. The previous thermal diffusion measurements[2,3] were made for the system of H_2–CO_2 at pressures up to 120 atm. In the present work, the H_2–A system has been selected so that a comparison could be made with the results obtained for the H_2–CO_2 system, the mass ratio of the molecules in the two cases being closely similar.

The measurements are made in a "two-bulb" type apparatus in which the top chamber is kept at a hot temperature T_t and the bottom one at a low temperature T_b. At a steady-state condition where the separation due to thermal diffusion is balanced by the remixing effect of the ordinary diffusion, the thermal diffusion factor α at a mean temperature $\overline{T}$ is expressed as follows:

$$\alpha(\overline{T})=\frac{\Delta x}{x_1 x_2 \ln(T_t/T_b)} \tag{1}$$

where x_1 and x_2 are mole fractions in feed of heavy and light components, respectively, and the thermal separation Δx is

$$\Delta x=(x_1)_b-(x_1)_t=(x_2)_t-(x_2)_b \tag{2}$$

where subscripts t and b show the top and bottom chambers, respectively, at the steady state, and Brown's expression[4] is used for $\overline{T}$:

$$\overline{T}=\frac{T_t T_b}{T_t-T_b}\ln\frac{T_t}{T_b} \tag{3}$$

1) T. Makita, *J. Soc. High Pressure Gas Industry* (Japan), **24**, 18 (1960)
2) T. Makita, *This Journal*, **29**, 47 (1960)
3) T. Makita, *ibid.*, **29**, 55 (1960)

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In this investigation, the thermal separation and the thermal diffusion factor have been calculated by Eqs. (2) and (1), respectively, at the mean temperature assigned by Eq. (3).

Experimentals

The experimental apparatus and procedures were described in details in the previous paper[2]. The top chamber was maintained in a boiling liquid bath, that is, *m*-xylene for 138.8°C, water for 100.0°C and carbon tetrachloride for 76.7°C were used, and the bottom chamber in a water thermostat of 25.0 or 30.0°C.

The sample gases used were obtained from commercial sources and purified by passage through a trap of silica-gel. The purity of both gases was more than 99.9%. The gas mixtures were made up in large cylinders and were used at least in one week.

A mixture of the sample gases was introduced into the evacuated chambers of the thermal diffusion apparatus which had been kept at each definite temperature. If necessary, the gas mixture was compressed through a pressure-intensifier in which the pressure was transmitted by by means of an oil-pump. After the gas mixture was allowed to attain to a steady state, the gas in each chamber was analysed. For the measurement at one condition, 3~4 runs were taken in about twice as long as time to attain to a steady state.

The composition of gas mixtures in feed and at equilibrium was determined both by chemical analysis and by use of a thermal conductivity bridge, which had been devised to obtain the accuracy within 0.02% of the composition.

Results and Considerations

The present experimental results are described and discussed on the effect of mean composition, temperature and pressure upon the thermal separation Δx and thermal diffusion factor α.

The effect of mean composition The thermal separation at the atmospheric pressure is plotted against the mean mole fraction of H_2, x_2, as isotherms of mean temperature in Fig. 1. It is found that the curves are a little more symmetrical than those obtained for the H_2-CO_2 system[2], and that the maximum separation is obtained near $x_2=0.55\sim0.60$ at the three temperatures. The composition of the maximum separation agrees with the results of Ibbs[5] at $\overline{T}=360°K$ and those of van Itterbeek *et al.*[6] at $\overline{T}=153.5°K$, being independent on temperature.

At the atmospheric pressure, the thermal diffusion factors are the same at the three temperatures and are nearly coincident with the results of Ibbs at $\overline{T}=360°K$, as shown in Fig. 2. The α increases gradually with increasing x_2, and reaches a maximum near $x_2=0.9$. In this figure,

4) H. Brown, *Phys. Rev.*, **58**, 661 (1940)
5) T. L. Ibbs, *Proc. Roy. Soc. London*, **A107**, 470 (1925)
6) A. van Itterbeek and A. de Troyer, *Physica*, **16**, 329 (1950)
7) T. Kihara, *Imperfect gases*, Asakura Book Co., Tokyo (1949)

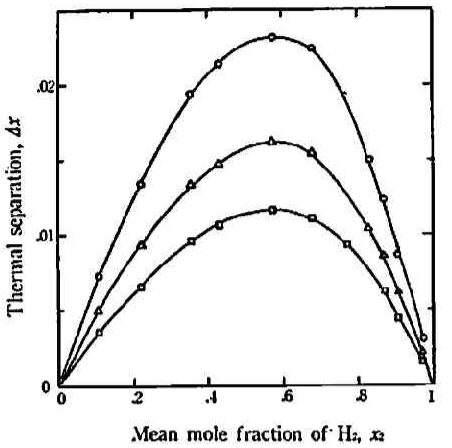

Fig. 1. Thermal separation versus mean mole fraction of H_2 diagram at the atmospheric pressur: ○ $\overline{T}$=349.0°K, △ $\overline{T}$=332.9°K, □ $\overline{T}$=322.7°K

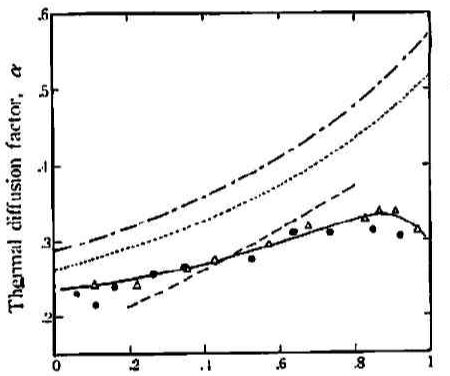

Fig. 2. Thermal diffusion factor as a function of mean mole fraction at the atmospheric pressure:
△ This work ($\overline{T}$=332.9°K),
● Ibbs[5] ($\overline{T}$=360°K)
---·--- Theoretical, (12-6) potential
····· Theoretical, (exp-6) potential
} ($\overline{T}$=332.9°K)
------ H_2–CO_2 system[2] ($\overline{T}$=346.0°K)

two theoretical curves are also plotted, which have been calculated from the first approximation of Kihara[1,7] by means of both Lennard-Jones (12–6) and a modified Buckingham (exp-6) potentials[8,9]. The force constants used are shown in Table 1[10]. The theoretical values are not satisfactory for the present system, but the (exp-6) potential gives somewhat better results than

Table 1

Parameter	Lennard-Jones A	Lennard-Jones H_2	Lennard-Jones mix.	modified Buckingham A	modified Buckingham H_2	modified Buckingham mix.
γm (Å)	3.87	3.287	3.58	3.866	3.337	3.574
ε/k (°K)	119.3	37.0	66.44	123.2	37.3	69.7
α	—	—	—	14.0	14.0	13.97

8) J. O. Hirschfelder, C. F. Curtiss and R. B. Bird, *The Molecular Theory of Gases and Liquids*, John Wiley & Sons, Inc., New York (1954)
9) E. A. Mason, *J. Chem. Phys.*, 22, 169 (1954)
10) E. A. Mason and W. E. Rice, *ibid.*, 22, 522, 843 (1954); E. A. Mason, *ibid.*, 23, 49 (1955)

the (12-6) one.

The results of the H_2-CO_2 system, which were shown as a dotted curve in Fig. 2, are steeper in slope than those of the H_2-A system. However, these two curves cross each other near $x_2=0.45$. It would be interesting to mention that the same value for α is given for both systems near $x_2=0.45$, and argon molecules are as effective as carbon dioxide molecules at the atmospheric pressure, though there is the much difference between their properties.

The results under high pressures are shown in Figs. 3 and 4. It can be seen that both Δx

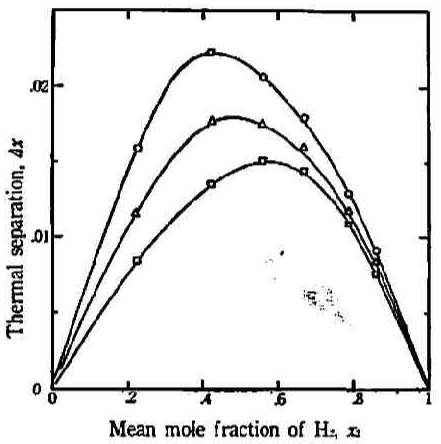

Fig. 3. Thermal separation versus mean mole fraction of H_2 diagram at $\overline{T}=335.8°K$ under varions pressures:
○ 108.7 atm, △ 53.6 atm □ 1.0 atm

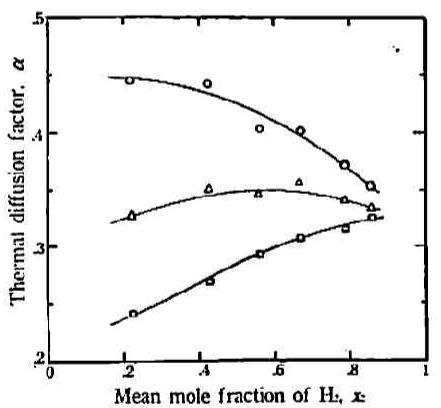

Fig. 4. Thermal diffusion factor at $\overline{T}=335.8°K$ under various pressure:
○ 108.7 atm, △ 63.6 atm, □ 1.0 atm

and α increase gradually with increasing pressure at a constant composition, and that the pressure effect becomes larger with decreasing x_2. That is, the composition of maximum separation displaces toward left with increasing pressure as shown in Fig. 3, and the slope of α versus x_2 at 108.7 atm is contrary to that of 1.0 atm. Although the tendency is similar to the system of H_2-CO_2 reported previously[2,3], the discrepancy in quantity is very large between them. For instance, the ration of α under 100 atm to α under 1 atm at a composition $x_2=0.3$ is about 6.8

11) T. L. Ibbs and K. E. Grew, *Proc. Phys. Soc.*, **41**, 456 (1929)
12) E. W. Becker, *Z. Naturforch.*, **5a**, 457 (1950)

for H_2-CO_2 and only about 1.7 for the H_2-A system. This means that the difference in properties between CO_2 and A molecules becomes remarkable under high pressure, although it is not at 1 atm as described above.

The effect of temperature The plots of the thermal separation against $\ln(T_t/T_b)$ at a constant composition are found to be linear at the atmospheric pressure. According to Eq. (1), the slope should be $x_1x_2\alpha$, and α at a constant composition is constant over the present temperature range. The experiments at low temperatures[6,11] gave considerably lower values of α. Some results are compared in Fig. 5, where it seems that α is constant at mean temperatures

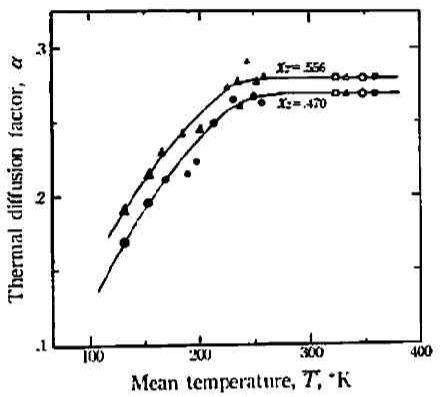

Fig. 5. Variation of thermal diffusion factor with mean temperature in H_2–A system at the atmospheric pressure:
○△□ This work, ■ Ibbs[5], ●▲ Ibbs-Grew[11] ⊙△ van Itterbeek *et al*[6]

above 250°K and decreases continuously at the lower temperatures.

The thermal separation of $x_2=0.561$ under pressures is plotted against $\ln(T_t/T_b)$ in Fig. 6. It can be seen that the relation is no longer straight under high pressures. And the thermal diffusion factor versus mean temperature diagram is also shown in Fig. 7, where α under high pressures decreases continuously with increasing $\overline{T}$. This tendency would be similar to the results obtained for the H_2-CO_2 system reported by Becker[12].

The effect of pressure The gas mixture with the composition of $x_2=0.561$, which has been close to the composition of maximum separation at the atmospheric pressure, is used for the measurement of the effect of pressure up to 220 atm. The results are given in Fig. 8, where

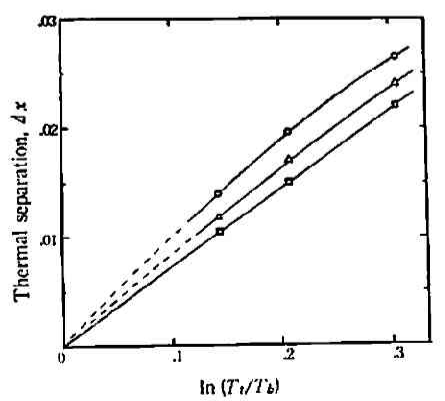

Fig. 6. Thermal separation versus $\ln(T_t/T_b)$ diagram of $x_2=561$ at varions pressures:
○ 98.1 atm, △ 49.6 atm, □ 1.0 atm

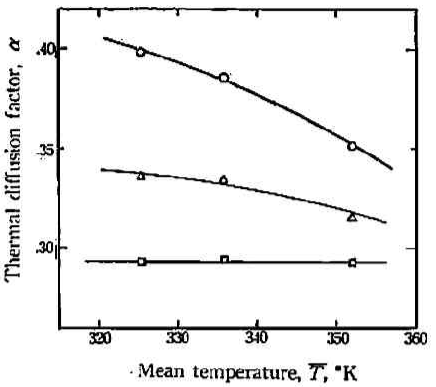

Fig. 7. Thermal diffusion factor as a function of mean temperature of $x_2=.561$ at various pressures:
○ 98.1 atm, △ 49.6 atm, □ 1.0 atm

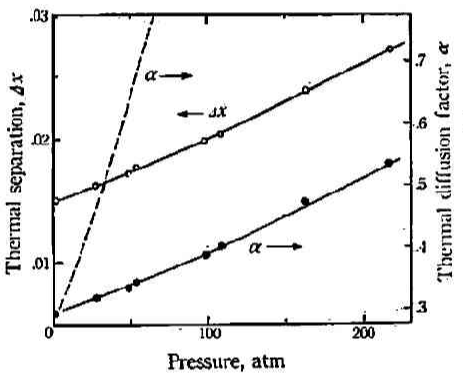

Fig. 8. Thermal separation and thermal diffusion factor as a function of pressure:
○ Δx } of H_2–A system, $x_2=.561$, $\overline{T}=335.8$°K
● α }
------ α of H_2–CO_2 system[2], $x_2=.491$, $\overline{T}=346.0$°K

a part of the results in the H_2-CO_2 system obtained previously[2] is also plotted by a dotted curve. As seen in this Figure, α of the H_2-CO_2 system becomes remarkablly large with increasing pressure, and, for instance, although the ratio of α at 115 atm to α at 1 atm was about 4.7 for the H_2-CO_2 system, that of α at 217 atm to α at 1 atm is only 1.8 for the H_2-A system. As the thermal diffusion is sensitive to the intermolecular force, the discrepancy between the two systems would be caused by the difference in properties between A and CO_2. The nature of interaction, which is the most important factor for the thermal diffusion under high pressure, has not been explained theoretically, and therefore now it would be reasonable to use the reduced state expression as a measure of the nature. And we must have more reliable experimental data for more systems.

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